Thermoelectric Properties of Self Assembled TiO_2/SnO_2 Nanocomposites

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Recent advances in improving efficiency of thermoelectric materials are linked to nanotechnology. Thermodynamically driven spinodal decomposition was utilized to synthesize bulk nanocomposites. TiO_2/SnO_2 system exhibits a large spinodal region, ranging from 15 to 85 mole % TiO_2. The phase separated microstructures are stable up to 1400 ^{o}C. Semiconducting TiO_2/SnO_2 powders were synthesized by solid state reaction between TiO_2 and SnO_2. High density samples were fabricated by pressureless sintering. Self assemble nanocomposites were achieved by annealing at 1000 to 1350 ^{o}C. X-ray diffraction reveal phase separation of $(Ti_xSn_{1-x})O_2$ type phases. The TiO_2/SnO_2 nanocomposites exhibit n-type behavior; a power factor of 70 W/mK^2 at 1000 ^{o}C has been achieved with penta-valent doping. Seebeck, thermal conductivity, electrical resistivity and microstructure will be discussed in relation to composition and doping.

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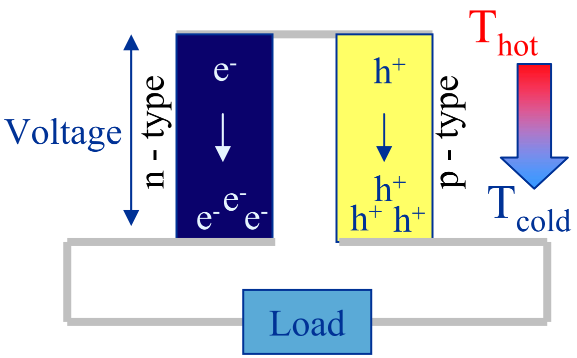
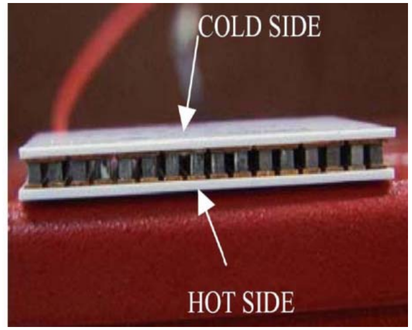
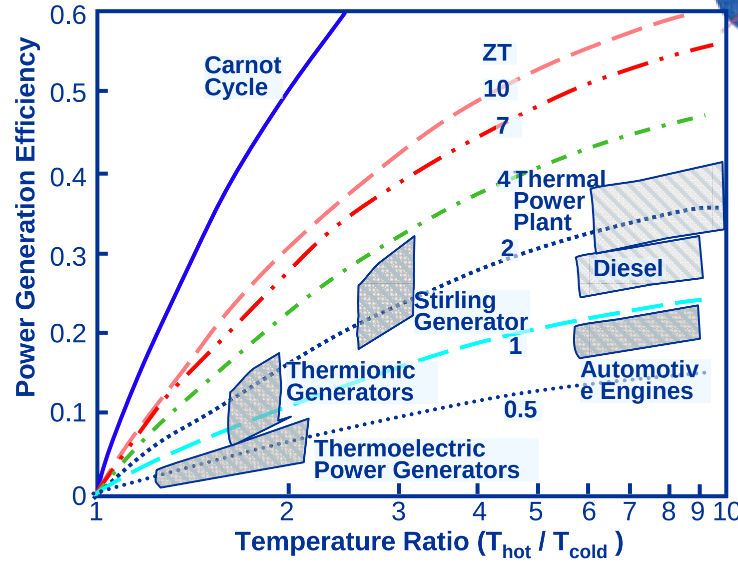
Program Support: NASA Radioisotope Power Systems

Heat to Electric Power Generation



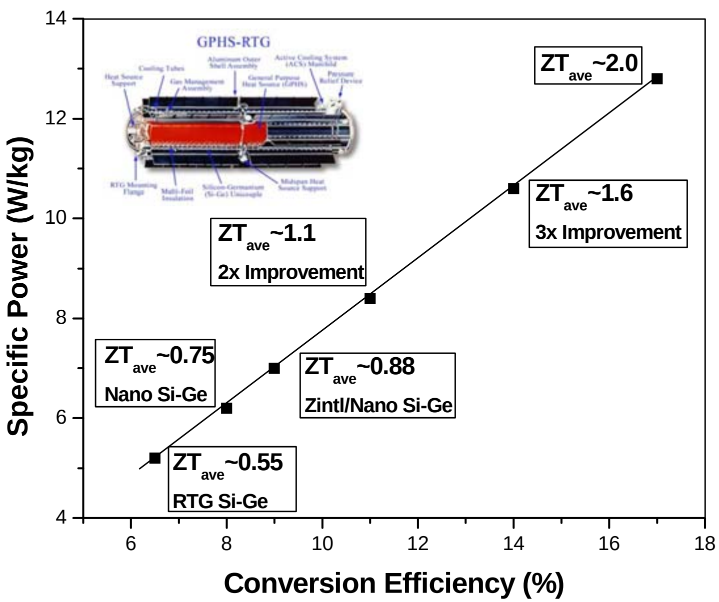




Objective: High Conversion Efficiency

●Reduces Mass, Volume & Cost

Space Power Generation



Waste Heat to Power

- Waste Heat is one of our most under utilized energy resources
- U.S.-energy consumption ~29 tera-kWh (10^{12}) Barrels of Oil – 170 giga-barrels (10^9)
- World-energy consumption ~120 tera- kWh (10^{12})
- 20-65 percent is lost in the form of heat
- Maximizes efficiency
- Reduces CO_2 emission

Nanotechnology

Figure of Merit

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

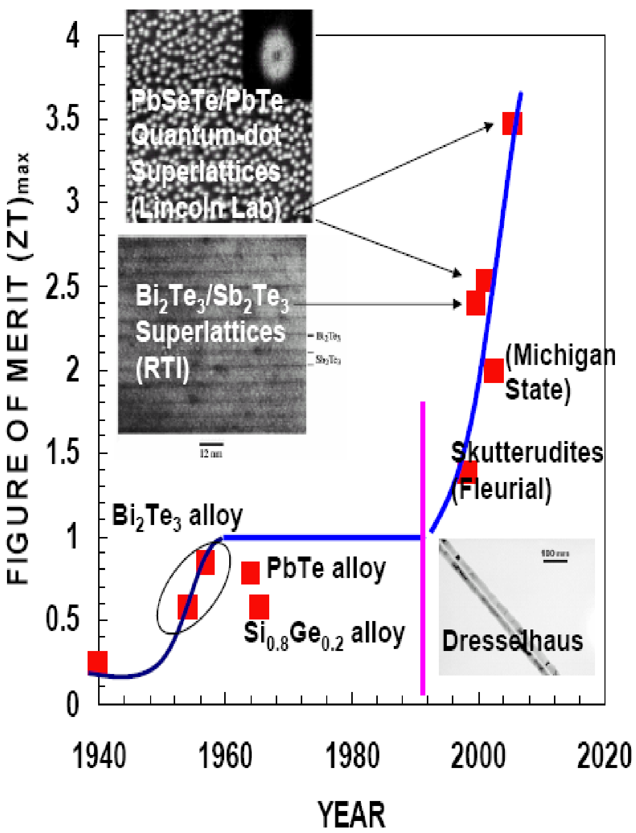
S - Seebeck coefficient
σ – electrical conductivity
κ– thermal conductivity

Efficiency

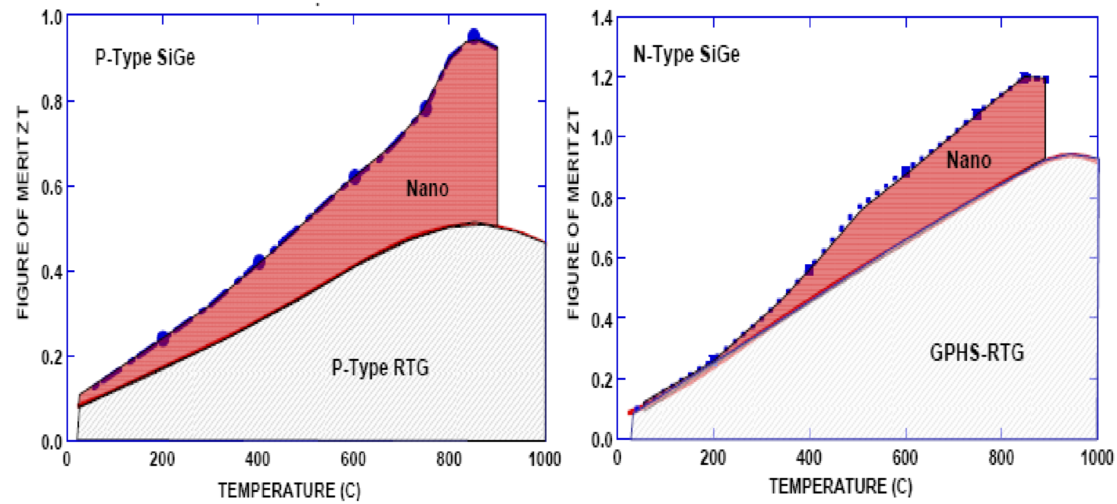
$$\eta_{max} = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + T_{cold}/T_{hot}}$$

Phonon Scattering:

- Atom disorder
- Alloying
- Anharmonic vibrations
- **Supperlattices**
- **Crystal Structures**
- **Nano-technology**



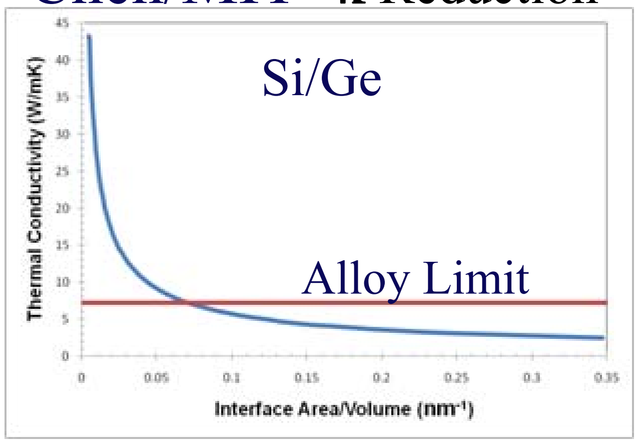
Fleurial/Chen – JPL/MIT



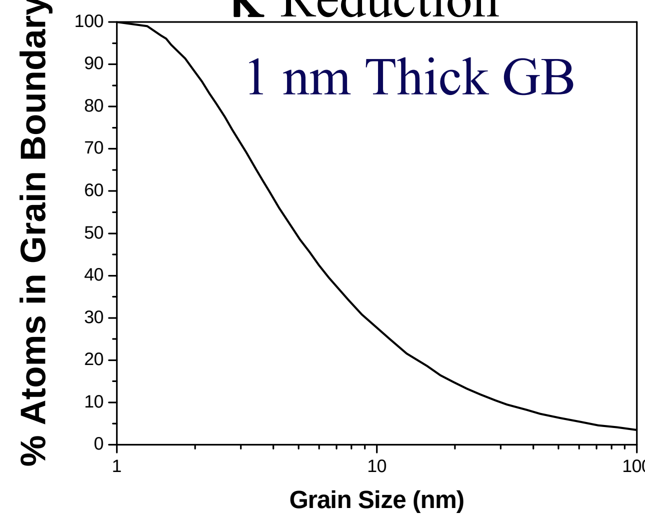
Fabrication of Nanostructure Solids

Goal: Preservation of the nanostructure during fabrication.

Chen/MIT- κ Reduction



κ Reduction



Nano-powder Synthesis

Thermal <u>Densification</u>
Pressure Assisted
Microwave
Laser
Plasma-SPS/P^2C

Cold <u>Densification</u>
Cold Spray
Dynamic Compaction
Plastic Deformation

<u>Inhibit Grain Growth</u>
- Rapid Thermal Process
- Inclusions

~~Nano-Powder~~

Post Process

<u>Thermodynamics</u>
Phase Transformation
Precipitation
Spinodal Decomposition

- Microstructure Dependent on Thermal Aging
- Composition Limited

Spinodal Decomposition

$TiO_2 - SnO_2$

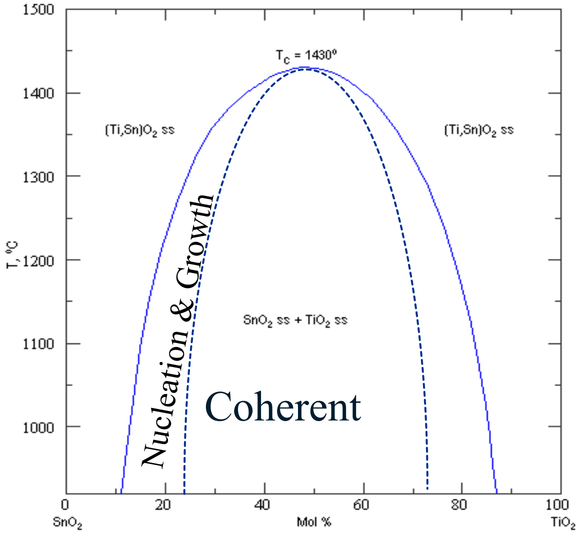


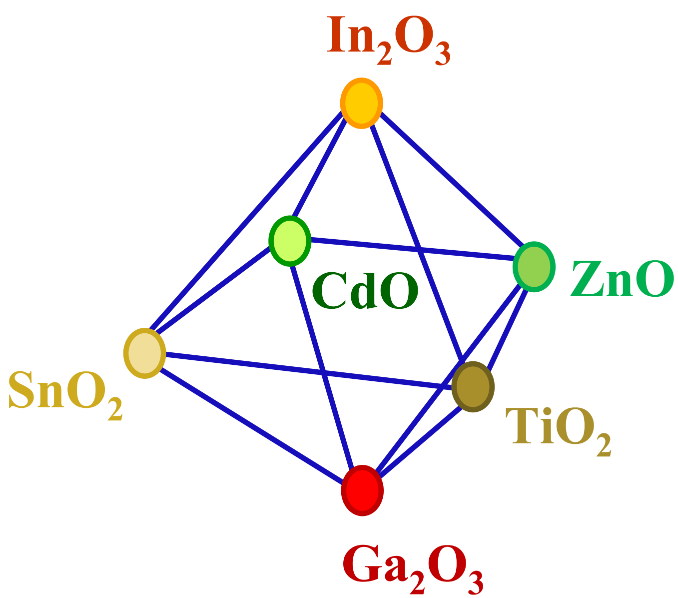
Fig. 10. TEM image of $(Ti_{0.5}/Sn_{0.5})O_2$ ceramics annealed for 48 h.

Desired Features

- ~50 nm grains
- High Temperature
- Wide Composition
- Large Δ Mass

Transparent Conducting Oxides

- Large Bandgap 2.4-3.8 ev
- N-type –Degenerate Semiconductor



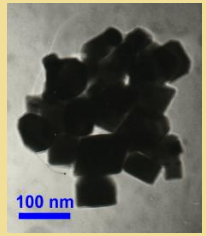
Electrical Conductivity

TCO	σ(S/m) @ RT
ITO	$8x10^5$
In_2O_3	$1x10^6$
SnO_2	$2.5x10^5$
ZnO	$8.3x10^5$
ZnO:Al	$7.7x10^4$
$CdSnO_2$	$7.7x10^5$
CdO:In	$1.7x10^6$
TiO_2	0.01

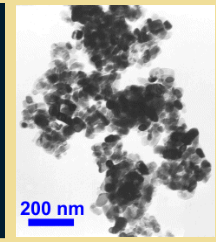
ZnO:Al
ZT=0.3 @ 1000 °C

Experimental

SnO_2
Purity: 99.9%
APS: 50 nm
SSA: 14.2 m^2/g



TiO_2 Rutile
Purity: 99.99 %
APS: 20 nm,
SSA: > 30 m^2/g



Dopants
CoO, MnO
Ta_2O_5, In_2O_3

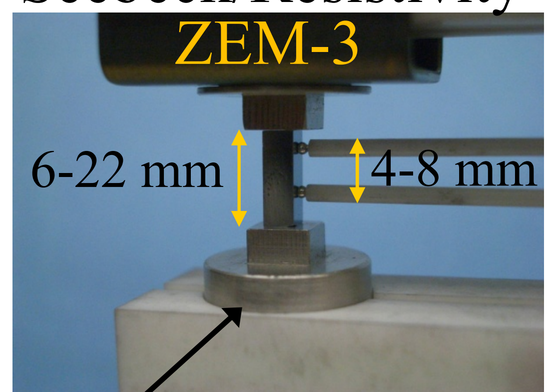
TiO_2/SnO_2
50/50 mol %
75/25 mol %
25/75 mol %

Powder Mixing

Compaction Die Press

Reactive Sintering 1250-1550 ^oC

Seebeck/Resistivity

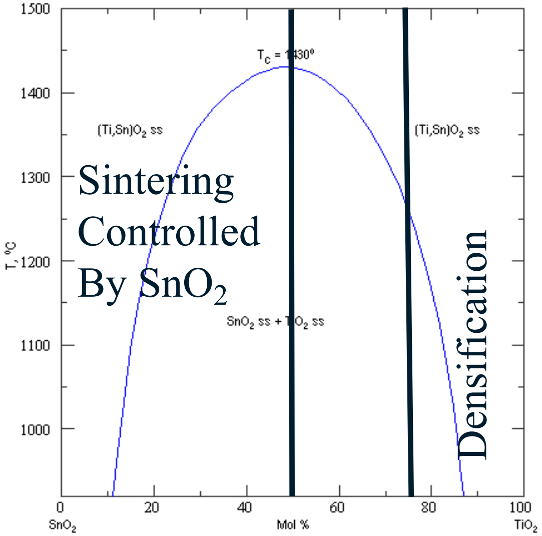


ΔT 0-50 ^oC/Furnace RT-1000 ^oC

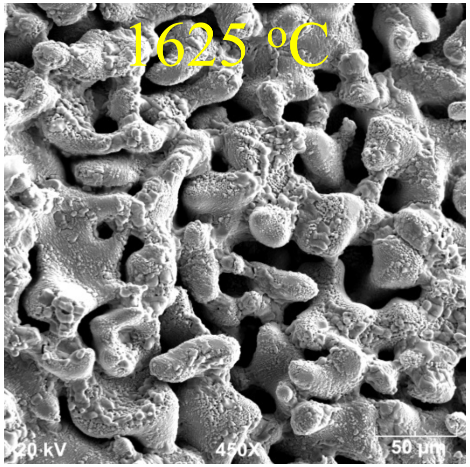
Thermal Conductivity

- **Laser Flash Method- Thermal Diffusivity**
- **Standard**
- **Specific Heat-Laser Flash**
- **Thermal Conductivity ($K = \alpha\rho C_p$)**

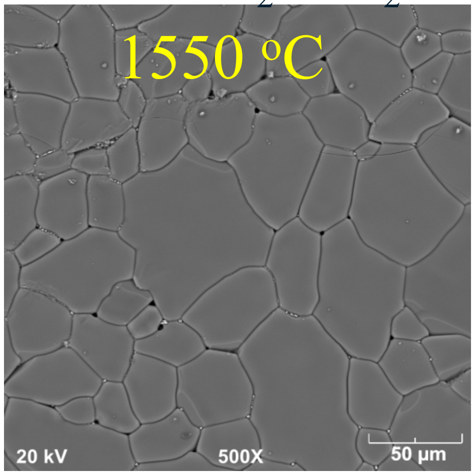
Sintering



50/50 TiO_2/SnO_2



75/25 TiO_2/SnO_2



Sintering-Inhibited

- Surface Diffusion <1100 °C
- Evaporation >1100 °C

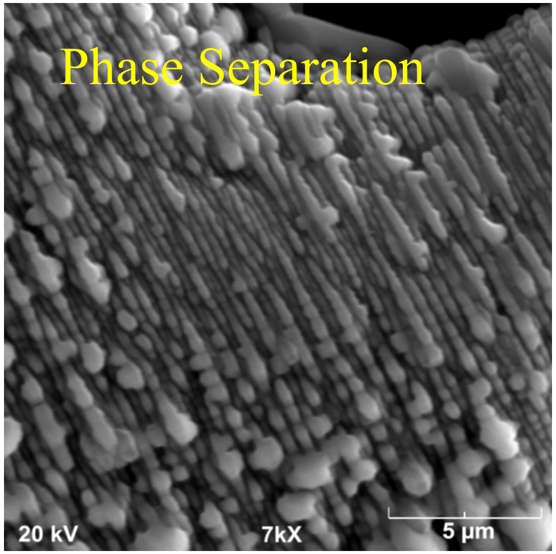
$SnO_2 \longrightarrow SnO + \frac{1}{2}O_{2\,(g)}$

Sintering Aids

- MnO, CoO, CuO, ZnO

$$CoO \rightarrow Co''_{Ti,Sn} + V_O^{\bullet\bullet}$$

50/50 TiO_2/SnO_2

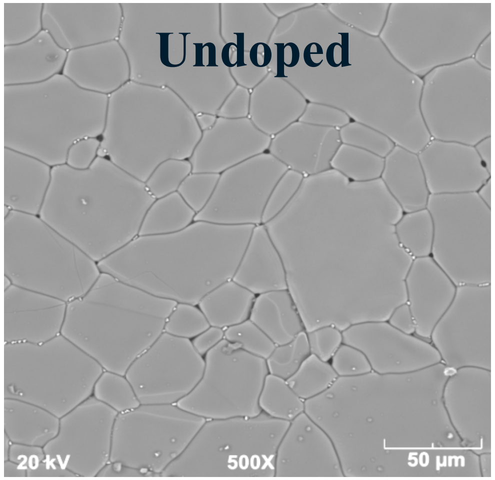


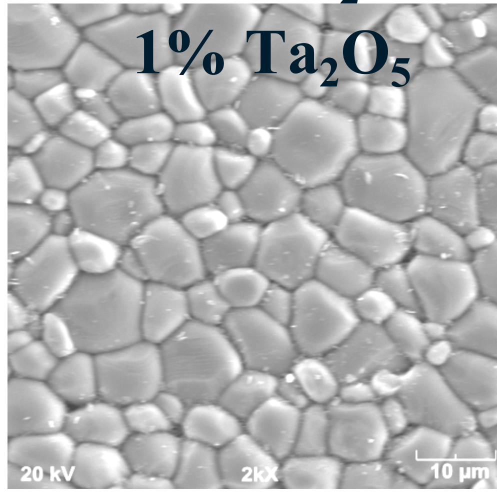
Ta_2O_5 & In_2O_3 Ineffective Sintering Aids

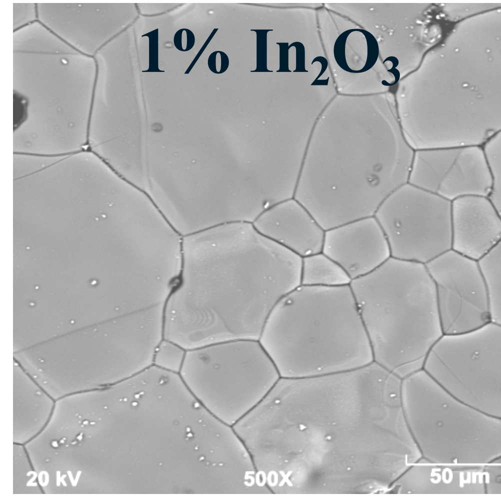
$$Ta_2O_5 \rightarrow 2Ta^{\bullet}_{Ti,Sn} + 2e' + \tfrac{1}{2}O_2$$

$$In_2O_3 \rightarrow 2In'_{Ti,Sn} + 2V_O^{\bullet}$$

75/25 TiO_2/SnO_2







XRD-Phases

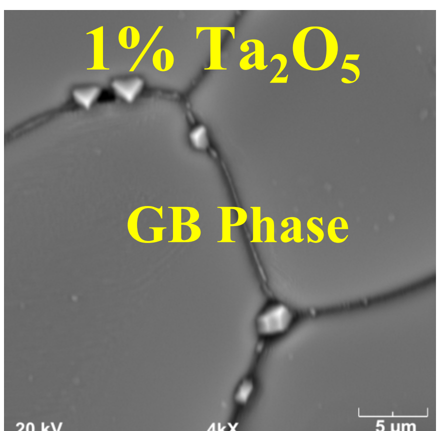
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
Reduced – TiO_2, Rutile
$(Ti_{0.8}Sn_{0.2})O_2$

XRD-Phases

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
Annealed – $(Ti_{0.8}Sn_{0.2})O_2$
1250 °C
Reduced – TiO_2, Rutile
$(Ti_{0.8}Sn_{0.2})O_2$

XRD-Phases

Sintered – TiO_2, Rutile
SnO_2, In_2O_3
Annealed – TiO_2, Rutile
1250 °C SnO_2, In_2O_3



Phase Separation

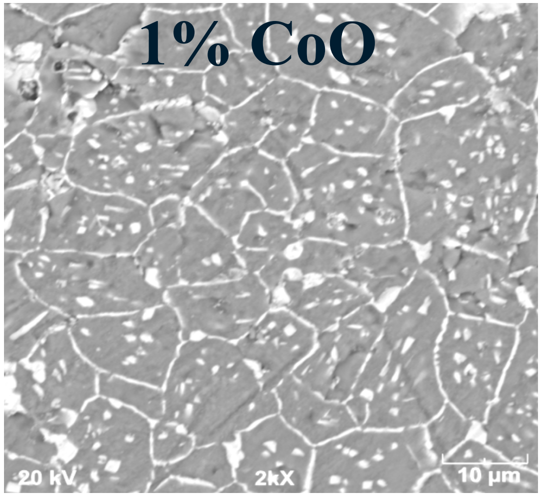
1% CoO XRD

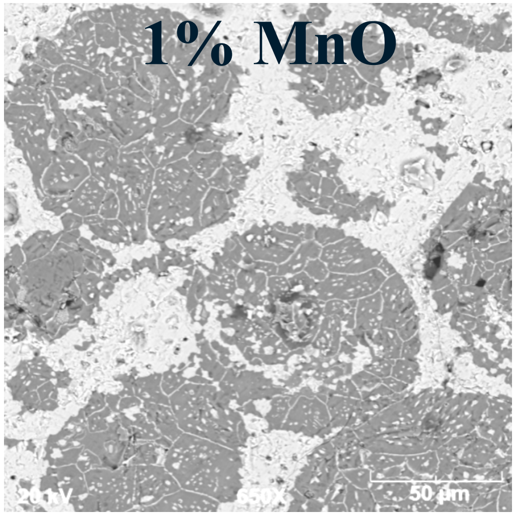
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_2$
Annealed – $(Ti_{0.9}Sn_{0.1})O_2$
1000 °C $(Ti_{0.1}Sn_{0.9})O_2$

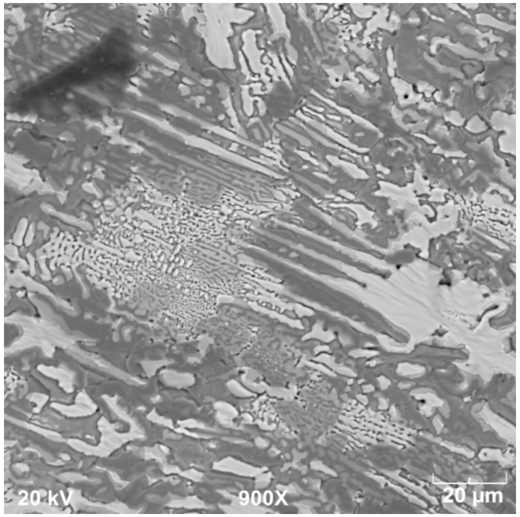
1% MnO XRD

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_2$
Annealed – $(Ti_{0.9}Sn_{0.1})O_2$
1000 °C $(Ti_{0.1}Sn_{0.9})O_2$

50/50 TiO_2/SnO_2







XRD-Phases

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_2$\
TiO_2
Annealed – $(Ti_{0.2}Sn_{0.8})O_2$
1000 °C $(Ti_{0.9}Sn_{0.1})O_2$

XRD-Phases

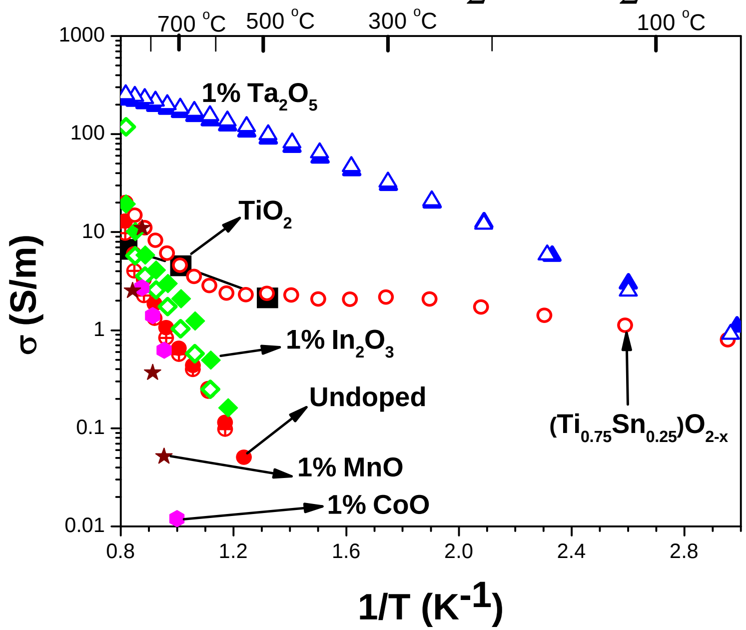
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.1}Sn_{0.9})O_2$
Annealed – $(Ti_{0.2}Sn_{0.8})O_2$
1000 °C $(Ti_{0.9}Sn_{0.1})O_2$

Microstructure Coarsening @ 1600 °C

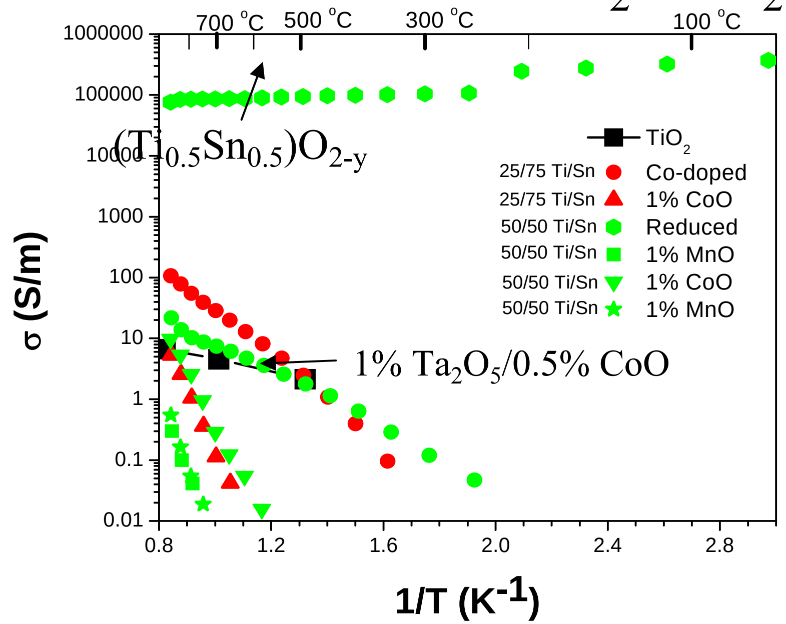
Grain Boundary Phases Segregation

Electrical Conductivity

75/25 TiO_2/SnO_2



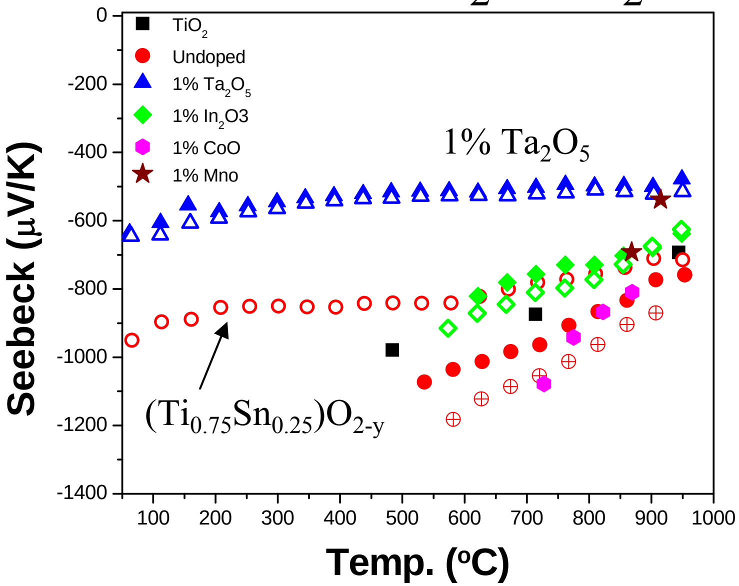
50/50 & 25/75 TiO_2/SnO_2



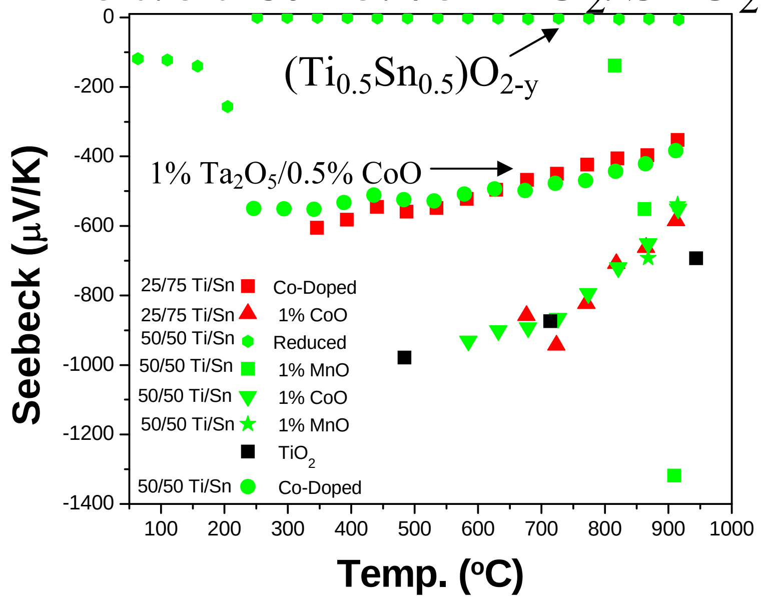
- Ta_2O_5 – Increases σ – E_a~0.25 ev
- $(Ti_xSn_{1-x})O_{2-y}$ – Oxygen Deficiency Increases σ – E_a~0.06 ev
- Co-doping-Ta_2O_5/CoO - Increases σ – E_a~0.5-0.7 ev
- In_2O_3, MnO & CoO – Ineffective in Enhancing σ – E_a~1-4.2 ev

Seebeck Coefficient

75/25 TiO_2/SnO_2

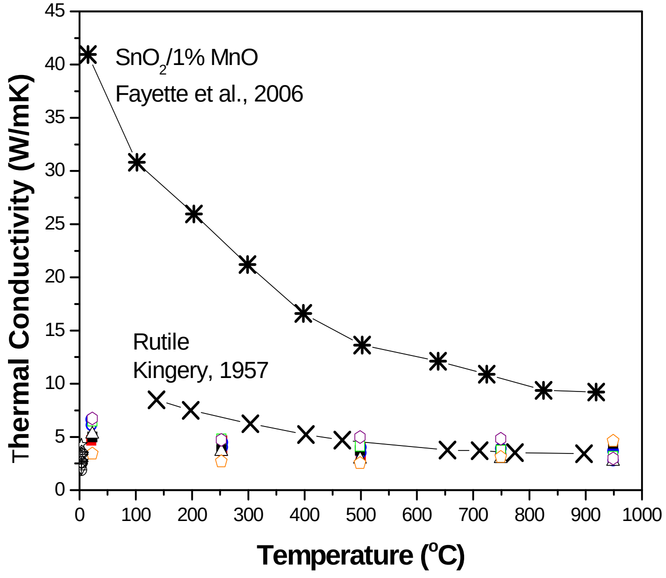


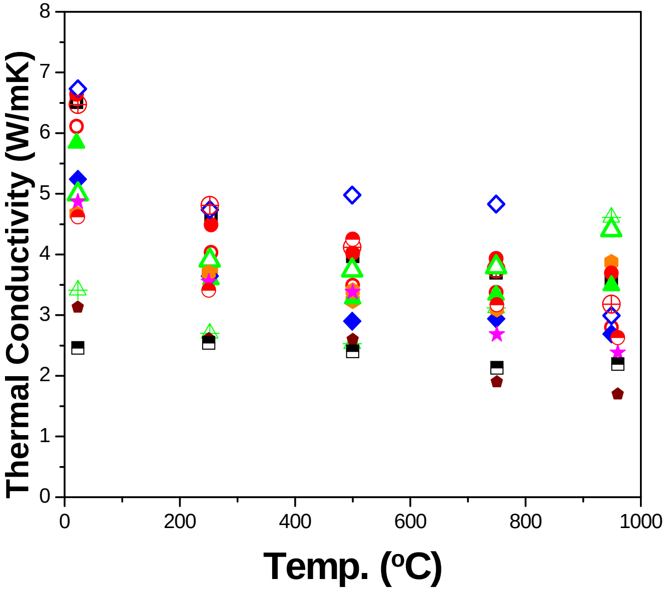
50/50 & 25/75 TiO_2/SnO_2



- N-type
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- $(Ti_{0.5}Sn_{0.5})O_{2-y}$ low Seebeck ~ 0

Thermal Conductivity





Compositions

- 1% MnO-50 TiO_2
- 1% CoO-50 TiO_2
- 1% MnO-75 TiO_2
- 1% CoO-75 TiO_2
- 1% MnO-25 TiO_2
- 1% CoO- 25TiO_2
- 1%Ta_2O_5/0.5% CoO-25 TiO_2

- •Compositions exhibit low κ – 1.7 to 6.8 W/mK
- •Observe no dependence on composition or post treatments
- •Spinodal Decomposition – κ reduction ?
- •Best ZT ~ 0.05

In Summary

•TiO_2/SnO_2 compositions exhibit low thermal conductivity. Reduction in thermal conductance by spinodal microstructure has not been isolated.

•Improvements in electrical conductivity is needed. Grain boundary phases could be detrimental. Ta_2O_5 or oxygen deficiency enhances electrical conductivity.

•Sintering aids are required to densify equal-molar and tin oxide rich compositions. MnO and CoO promoted phase separation.